

# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Preparation of Ashless Lubricant Additives Additives thus prepared and Lubricants Containing them

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a Company organised under the Laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the preparation of lubricant additives which do not leave ash upon combustion or decomposition and which have good detergent properties.

According to the invention these additives are prepared by reacting an olefin polymer which carries as substituents at least two succinic acid groups, succinic anhydride groups or succinic halide groups, with a polyhydric alcohol.

The polyolefin chain may consist of monomeric units of the same olefin or of monomeric units of different olefins. Examples are polyethylene, polypropylene, polybutene and polyisobutene chains, polyolefin chains which have been built of the monomeric units ethylene and propylene, or propylene and butene, or butene and isoprene, and polyolefin chains which contain units originating from substituted olefins, for example, styrene.

The number of carbon atoms of the polyolefin chain must be such that the additive is soluble in lubricants. The chain length required for this purpose can easily be determined experimentally. It may be taken as a general rule that a chain of such length as to have, on an average, 50 carbon atoms per polar group, is sufficient.

This is termed the relative chain length. Raising the relative chain length increases the solubility. Upon raising the absolute chain length, however, a stage is reached where the solubility begins to decrease. The largest

absolute chain length usable in this respect depends, amongst other factors, on the degree of branching of the chain and on its crystallinity. A compound with a fully atactic polypropylene chain will be better soluble than a compound with an isotactic polyethylene chain at otherwise equal chain length. For compounds with a hydrocarbon chain of more than 50,000 carbon atoms a poor solubility in the lubricant can usually be expected.

As appears from the foregoing, the number of polar groups also influences the solubility. In view of the hydrophilic character of the polar group it is understandable that upon increase of the number of these groups in the additive molecule the oil-solubility will eventually become very poor. As already indicated, the additives preferably have at least 50 carbon atoms per polar group in the polyolefin chain. A very suitable ratio of chain length to number of polar groups is one polar group to an average of 100 to 400 carbon atoms in the polyolefin chain.

The polyhydric alcohol may have branched or unbranched carbon chains. Suitable polyhydric alcohols are dihydric alcohols, such as glycol, 1,2-dihydroxypropane, 1,3-dihydroxypropane, the dihydroxybutanes, the dihydroxypentanes; trihydric alcohols, such as glycerol, the trihydroxybutanes, the trihydroxypentanes; corresponding alcohols with more hydroxyl groups, for example, the tetritols, pentitols and hexitols, which are related to the sugars.

Preferably the polyhydric alcohol has at least three hydroxyl groups, pentaerythritol and mannitol being particularly suitable.

The additives may be prepared according to any method suitable for this purpose. Preferred methods start from an olefin polymer which may be either a homopolymer or a copolymer and in which active functions are present which render a reaction with maleic

anhydride, maleic acid or maleic halide possible, in such a way that a polymer is formed with succinic anhydride, succinic acid or succinic halide groups, after which these groups are completely or partly esterified with a polyhydric alcohol.

Suitable starting materials are, for example, olefin polymers which have several double bonds, or several halogen atoms which can be split off as hydrogen halide with formation of double bonds. For instance, a copolymer of isobutene and isoprene is taken as a starting material, on to which maleic anhydride is added. The product obtained which may be described as a hydrocarbon chain carrying succinic anhydride groups, is subsequently caused to react with a polyhydric alcohol, for example a glycol, a trihydric alcohol or an alcohol with more hydroxyl groups, such as pentaerythritol. Another example is the reaction of a chlorinated copolymer of ethylene and propylene with maleic anhydride, followed by conversion with a polyhydric alcohol. In the reaction of the anhydride with the chlorinated copolymer hydrogen chloride is split off and the maleic anhydride reacts with the unsaturated copolymer formed with formation of succinic anhydride groups which are linked to the copolymeric chains.

In both procedures mentioned the reaction of the unsaturated copolymer or the chlorinated copolymer, with maleic anhydride results in a reaction product in which the number of double bonds of the hydrocarbon chain has remained unchanged, or corresponds with the number of molecules of hydrogen halide split off. If desired, these double bonds can be converted into single bonds by hydrogenation, which is preferably performed before carrying out the esterification.

In the reaction of the olefin polymer containing succinic groups with the polyhydric alcohol a mixture of monoesters and diesters is formed upon application of an underdose (i.e. less than the stoichiometric amount) of polyhydric alcohol; cyclic compounds may also be formed, because two hydroxyl groups of one molecule of polyhydric alcohol form ester compounds with the two carboxyl groups of the same succinic acid group or anhydride group. If, however, an underdose of polyhydric alcohol is applied the ester formation may be attended with interlinking of two or more polyolefin chains. If this interlinking occurs to a high degree, the solubility of the additive in lubricants may be reduced. Therefore, the application of a quantity of polyhydric alcohol is preferred which is at least sufficient for the conversion of all succinic anhydride groups or succinic acid groups into succinic diester groups, because in that case there is not much chance of excessive interlinking of chains. An excess of polyhydric alcohol, calculated on the stoichiometric quantity, is preferred.

The reaction of maleic anhydride with an

olefin polymer with several double bonds or of maleic anhydride and a chlorinated polyolefin is carried out at elevated temperature, for example at temperatures above 120°C. Temperatures between 150 and 200°C are preferred. At these temperatures the hydrogen halide is easily split off from the chlorinated polyolefin and the maleic anhydride readily reacts with the unsaturated polyolefin.

The reaction of the resultant product with the polyhydric alcohol is carried out at elevated temperature. A temperature between 100 and 250°C is very suitable. As complete esterification of the anhydride groups is accompanied by the formation of water, the reaction, is preferably performed in such a way that the reaction water is removed at once, for example, by employing a solvent which forms an azeotrope with water, or by employing an inert gas as a water-removing agent.

However, any known measure for the preparation of an ester of an organic acid may be employed.

If desired, the products may be mixed with a small quantity of oil, resulting in a concentrate which may be used for the preparation of lubricants containing additives. If desired, this quantity of oil may already be added to the reactants before the reaction.

The products may be used as additives for lubricants of various kinds, such as mineral lubricating oils. However, synthetic lubricating oils may also be used, as well as lubricating oils containing fatty oils. The products may also be incorporated in lubricating greases.

The proportions in which the products may be added to lubricants may vary within wide limits. In general, the desired improvement in the behaviour of the lubricant is brought about if the quantity added amounts to between 0.1 and 5 per cent by weight, in particular to 1 to 3 per cent by weight, of the finished lubricant. In special cases larger quantities, e.g. more than 10%w may be added, for example, for use in diesel engines in which a high degree of fouling occurs.

Further, two or more of these products may be used together with each other, or the products may be used together with other additives, such as antioxidants, detergent additives, viscosity-index improvers, anti-corrosives, anti-fouling agents, pour-point reducers and oiliness agents.

The following example illustrates the invention.

#### EXAMPLE

As starting material an ethylene-propylene rubber was taken with a molecular weight of 150,000 and a monomer ratio of 1:1 (molar) which had been chlorinated to a chlorine content of 1.42%w.

A quantity of 4.6 parts by weight of maleic anhydride was dissolved in 18 pbw of o-dichlorobenzene. This solution was added to a

- solution of 90 pbw of the chlorinated ethylene-propylene rubber in 700 pbw of o-dichlorobenzene which was kept at a temperature of 180°C in a nitrogen atmosphere. After 20 hours heating at this temperature with stirring, the temperature of the mixture was raised to 200°C, after which 9.8 pbw of pentaerythritol were added. After heating for 24 hours at this temperature with stirring the solvent was removed by vacuum distillation. The residue was incorporated in an equal volume of toluene. After filtration the filtrate was poured into five times its volume of methanol which contained 10%w of water. The insoluble part that separated was taken up in an equal volume of toluene, after which the resultant solution was poured into five times its volume of methanol which contained 10%w of water. The insoluble part that separated was liberated from any solvent and water left by vacuum distillation. The yield was 98.1 pbw.
- The product of the example was tested as a 1.5%w solution in a base oil in a single-cylinder Gardner diesel engine and in a single-cylinder Petter gasoline engine (GARDNER and PETTER are trade marks).
- In both engine tests the base oil was a solvent-refined paraffinic lubricating-oil distillate. In the Gardner test the viscosity of the base oil was 11.5 cS at 98.9°C; in the Petter test it was 7.2 at 98.9°C.
- Gardner diesel engine.* Water-cooled single-cylinder four-stroke engine, bore 108 mm, stroke 152.4 mm, piston displacement 1.4 litres, power output 11 hp at 1200 rpm (60 mg of fuel per power stroke). The test duration was 17 hours. The fuel was a gas oil with a sulphur content of 0.9%w. The cooling-water temperature was 80°C.
- In this test the degree of piston fouling was rated.
- Petter gasoline engine.* Water-cooled single-cylinder four-stroke engine, bore 85 mm, stroke 82.5 mm, piston displacement 468 cm<sup>3</sup>, compression ratio 10.0:1. The test was carried out under varying conditions, namely alternately 55 minutes at 1500 rpm, 3.5 hp load and a mixture strength of 1.0 and 5 minutes at 1200 rpm, 2 hp load and a mixture strength of 1.9. The test duration was 48 hours. The fuel was a premium gasoline with 0.4 ml TEL (tetraethyl lead 61.48%w, ethylene dibromide 17.86%w, ethylene dichloride 18.81%w, colouring matter 0.06%w, kerosine and impurities 1.79%w), per litre (F-1 octane number ca 100) and a sulphur content of 0.10%w. The temperature of the cylinder cooling water was 80°C, the temperature of the cooled timing gear cover was 25°C.
- In this engine the degree of sludge formation was rated.
- The results of these engine tests are recorded in the table below.

TABLE

	Gardner-engine test piston cleanliness (10=clean)	Petter-engine test sludge rating (10=clean)
65		
	Additive applied	
70	none	5.6
	additive of the example	8.7
		8.4
	WHAT WE CLAIM IS:—	
75	1. A process for the preparation of an ashless lubricant additive containing an oleophilic hydrocarbon chain and at least two polar groups, comprising reacting an olefin polymer which carries as substituents at least two succinic acid groups, succinic-anhydride groups or succinic halide groups, with a polyhydric alcohol.	
80	2. A process according to Claim 1 wherein the length of the polyolefin chain corresponds with an average of at least 50 carbon atoms per polar group.	
85	3. A process according to Claim 2 wherein the length of the polyolefin chain corresponds with from 100 to 400 carbon atoms per polar group.	
90	4. A process according to any of Claims 1 to 3 wherein the polyolefin chain has not more than 50,000 carbon atoms.	
	5. A process according to any of Claims 1 to 4 wherein the polyhydric alcohol contains at least three hydroxyl groups.	
	6. A process according to Claim 5 wherein the polyhydric alcohol is pentaerythritol.	
	7. A process according to any of Claims 1 to 6 wherein the reaction temperature is from 100 to 250°C.	
	8. A process according to any of Claims 1 to 7 wherein at least the stoichiometric quantity of polyhydric alcohol is applied.	
	9. A process according to Claim 8 wherein an excess of polyhydric alcohol is applied.	
	10. A process for the preparation of an ashless lubricant additive substantially as described.	
	11. A lubricant additive which has been prepared by a process as claimed in any of Claims 1 to 10.	
	12. A lubricant composition comprising a	

major proportion of a lubricant and a minor proportion of a lubricant additive as claimed in Claim 11.

13. A lubricant composition as claimed in  
5 Claim 12 and substantially as described.

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